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Reverse Osmosis Separations of Some Inorganic Solutes in Ethanol Solutions Using Cellulose Acetate Membranes*

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Abstract

Reverse osmosis separations of 20 inorganic solutes from ethanol solutions were studied by using porous cellulose acetate membranes. The experimental results were analyzed by basic transport equations developed by Kimura and Sourirajan. On the basis of the above analysis the free energy parameters of ions were calculated and compared with the values obtained from water and methanol solvent systems. The study confirms that the difference in the free energy parameters among univalent cations and univalent anions is widened in the solvent of a lower dielectric constant; such an enhanced difference is further reflected in the increase of the difference among inorganic solute separations from the solvent of a lower dielectric constant. Consequently, fractionation of inorganic solutes can be performed more easily in ethanol solvent than in water and in methanol solvent.

INTRODUCTION

The removal of trace inorganic and organic solutes from nonaqueous solvents using reverse osmosis membranes is a newly opened field of

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membrane separation process. Though it is of practical interest in view of the separation and purification of nonaqueous solution systems as well as of fundamental interest in view of the change in the interaction forces working in the membrane material–solute–solvent systems and the change in the average pore size and pore size distribution of the membrane under the different solvent environment, only a few works can be found in the literature (*1–3*) on this subject. Our previous work on the separation of inorganic and organic solutes from methanol solvent by porous cellulose acetate membranes demonstrated that almost complete removal of inorganic solutes involving divalent ions is feasible (*4–6*). As expected, the interaction forces working in the membrane material–solute–solvent system are significantly different in water solvent and in methanol solvent, as indicated by the sequence of retention volume data from liquid chromatography experiments, the difference being further reflected in the change in parameters governing membrane separation, such as free energy parameters of ionic solutes and the interaction force constants of inorganic and organic solutes.

Considering the sequence of the dielectric constants at 25°C of water (78.54), methanol (32.63), and ethanol (24.30), a natural extension of the above works seems to be the reverse osmosis separation of inorganic and organic solutes from ethanol solvent. In the present work, therefore, the reverse osmosis separation of the combination of eight cations and seven anions dissolved in ethanol solutions is studied. The reverse osmosis data obtained are analyzed by Kimura-Sourirajan's transport equations to determine the solute transport parameter for each inorganic solute studied. The latter parameter is further decomposed into the ionic free energy parameter applicable to the system involving cellulose acetate (CA E-398)–ethanol solvent. Our interest is particularly focused on the change in the free energy parameter of ions with the sequential change of solvent from water to ethanol, since the free energy parameter reflects the interaction forces working in the membrane material–solute–solvent systems. Such information should be of fundamental importance to the surface science of polymeric material in different solvent environments and also may lead to a prediction technique for the separation of inorganic solutes from solvents of different dielectric constant.

EXPERIMENTAL

All inorganic chemicals used in this study were of ACS reagent grade. Absolute ethanol (99.96%) supplied by Commercial Alcohols Ltd. was used and it was isolated from the atmosphere while being used in the reverse osmosis experiments. The apparatus and experimental details were the same as those reported earlier (*4–6*). Batch 316 (10/30) cellulose acetate (E-398-3) membranes were prepared according to the description of Pageau and Sourirajan (*7*), and their surface porosities were varied by shrinking the membrane in water at temperatures from 65 to 95°C. The membranes were solvent exchanged to ethanol solutions by successive immersion in ethanol–water solutions which were progressively more concentrated in ethanol. They were then loaded into reverse osmosis flow-type cells and pressurized at 2068 kPag (= 300 psig) for 3 h. The operating pressure for all subsequent experiments was 1724 kPag (= 250 psig) and the solution temperature was fixed at 25°C. A set of specification of the membranes used is given in Table 1 in terms of pure solvent permeability constant A (in kg·mol of ethanol /$m^2 \cdot s \cdot kPa$), solute transport parameter (treated as a single quantity, m/s) for LiCl at 250 psig and 0.15 molal feed concentration, which were calculated by applying the basic transport equations (*8*). The reason for the choice of LiCl as the reference solute for the specification of the membrane is its greater solubility in ethanol solvent when compared to NaCl solute and the consequent higher accuracy in the analysis.

Except LiCl experiments for the purpose of membrane characterization, all the RO experiments were conducted in the feed concentration range of ~0.001 molal. For each experiment, the pure solvent permeation rate (*PSP*), the membrane permeated product rate (*PR*), and the solute separation (f), defined as

$$f = \frac{\text{feed solution molality} - \text{product solution molality}}{\text{feed solution molality}} \tag{1}$$

were determined.

The concentration of the LiCl solutions was determined by electrical conductance, NH_4Cl solutions by nitrogen analyzer (Dohrman model DN-100), and the rest of the inorganic solutes were analyzed by atomic absorption spectroscopy.

RESULTS AND DISCUSSION

Basic Transport Equations

The reverse osmosis experimental data were analyzed by the following transport equations derived elsewhere (*8*),

TABLE 1
Membrane Specifications

Membrane no.	1	2	3	4	5	6
1724 kPag (= 250 psig). Pure solvent permeability constant, $A \times 10^7$ $\left(\frac{\text{kg}\cdot\text{mol ethanol}}{\text{m}^2\cdot\text{s}\cdot\text{kPa}}\right)$	0.361	0.445	0.597	0.465	0.619	0.759
Solute transport parameter, $(D_{AM}/K\delta)_{LiCl} \times 10^7$, m/s	1.311	1.635	2.081	2.325	2.507	3.647
$\ln C^*_{NaCl}$	−9.837	−9.616	−9.375	−9.264	−9.189	−8.814
LiCl separation, %[a]	96.1	97.3	96.5	90.2	94.2	91.5
Product rate $\times 10^3$, kg/h[a]	13.51	17.55	22.69	17.33	24.33	28.35

[a] Effective membrane area, 13.2×10^{-4} m^2; feed LiCl concentration, 9.453×10^{-4} molal.

$$A = \frac{(PSP)}{M_B \cdot S \cdot 3600 \cdot P} \tag{2}$$

$$N_B = A(P - \pi_2 + \pi_3) \tag{3}$$

$$= (D_{AM}/K\delta)c\,\frac{1 - X_{A3}}{X_{A3}}\,(X_{A2} - X_{A3}) \tag{4}$$

$$= kc(1 - X_{A3})\ln\left(\frac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}}\right) \tag{5}$$

All symbols are defined at the end of this paper. Equations (2) to (5) can be used to calculate the pure solvent permeability constant A, solute transport parameter $D_{AM}/K\delta$, and mass transfer coefficient k from a set of experimental reverse osmosis data, (PSP), (PR), and $f(8)$. Such calculations were performed when membranes were characterized by the reverse osmosis data with respect to LiCl solute. The physicochemical data required for such calculations are listed in Table 2, and A and $D_{AM}/K\delta$, parameters which characterize the membranes used in this study, are listed in Table 1.

The above calculation enables one to obtain the mass transfer coefficient k corresponding to the feed LiCl concentration used in the experiment. The mass transfer coefficient k so obtained can be related to the one correspond-

TABLE 2

Physicochemical Data of LiCl–Ethanol Solutions Pertinent to Calculation of Reverse Osmosis Transport Equations[a]

Molality	Mole fraction × 10^3	Osmotic[b] pressure (kPa)	Diffusivity[c] × 10^{10} (m^2/s)	Molar density (mol/m^3)
0	0	0	4.92	17.14
0.3	13.6	793	3.89	—
0.5	22.5	1425	4.15	—
1.0	44.0	3310	5.46	—
1.5	64.5	5913	—	—
2.0	84.2	9473	—	—

[a] Data at 25°C.

[b] Calculated using osmotic coefficient in Ref. *9*.

[c] Calculated using the Nernst-Haskell equation (*10*).

ing to the dilute feed solution by using the Schmidt-Sherwood correlation (*11*),

$$k_{\mathrm{LiCl,dil}} = k_{\mathrm{LiCl}} \left\{ \frac{(D_{AB})_{\mathrm{LiCl,dil}}}{(D_{AB})_{\mathrm{LiCl}}} \right\}^{2/3} \tag{6}$$

where $(D_{AB})_{\mathrm{LiCl,dil}}$ and $(D_{AB})_{\mathrm{LiCl}}$ designate the diffusivity of LiCl solute at infinite dilution and that corresponding to the feed LiCl concentration. Likewise, $k_{\mathrm{LiCl,dil}}$ and k_{LiCl} designate the mass transfer coefficient of LiCl solute at infinite dilution and that corresponding to the feed LiCl concentration. Furthermore, correlating $k_{\mathrm{LiCl,dil}}$ to A, a linear relationship represented by

$$k_{\mathrm{LiCl,dil}} = 49.51A + 5.962 \times 10^{-6} \tag{7}$$

was found to be valid.

With respect to the other inorganic solutes, the reverse osmosis experiments were carried out using dilute feed solution (~0.001 molal). Therefore, the effect of the osmotic pressure can be ignored so that (*PR*) is approximately equal to (*PSP*). In such a case Eqs. (2) to (5) can be simplified to (*12*),

$$(D_{AM}/K\delta) = \frac{(PSP)}{3600 \cdot S \cdot \rho} \, \frac{1-f}{f} \left[\frac{(PSP)}{3600 \cdot S \cdot \rho \cdot k} \right]^{-1} \tag{8}$$

In order to use Eq. (8) for the calculation of $D_{AM}/K\delta$, a numerical value for the mass transfer coefficient k is required. The Schmidt-Sherwood correlation is again applicable and in analogy to Eq. (6),

$$k = k_{\mathrm{LiCl,dil}}[D_{AB}/(D_{AB})_{\mathrm{LiCl,dil}}]^{2/3} \tag{9}$$

can be used for the calculation of k together with the information on the diffusivity D_{AB} data for the different inorganic solutes listed in Table 3.

Free Energy Parameter

For the case of completely dissociated electrolytes, the solute transport parameter can be written in terms of ionic contribution to the free energy parameter as (*13–15*),

TABLE 3
Data on Diffusivity of Various Inorganic Solutes in Ethanol Solvent at Infinite Dilution and at 25°C

Inorganic solute	Diffusivity $\times 10^{10}$ (m^2/s)
LiCl	4.92
LiBr	5.03
NaCl	5.62
NaBr	5.77
NaI	6.03
KF	5.44[a]
KCl	6.15
KBr	6.32
KI	6.63
RbBr	6.56
RbI	6.89
CsCl	6.62
CsBr	6.80
CsI	7.19
NH_4Cl	5.71
$CaCl_2$	4.60[a]
$SrCl_2$	4.60[a]
$NaNO_2$	5.779
$NaClO_3$	6.075
$NaClO_4$	6.407

[a] Assumed on the basis of diffusivity in methanol solutions.

$$\ln (D_{AM}/K\delta) = \ln C^*_{\text{NaCl}} + \{n_c(-\Delta\Delta G/\mathbf{R}T)_{c^+} + n_a(-\Delta\Delta G/\mathbf{R}T)_{a^-}\} \tag{10}$$

where ln C^*_{NaCl} is a parameter which represents the porosity of the membrane surface and $\Delta\Delta G$ designates the surface excess free energy of solvation of the cation (c^+) or the anion (a^-) and n_c and n_a are the number of moles of cations and anions, respectively, arising from the dissociation of one mole of solute. The surface excess free energy $\Delta\Delta G$ is defined by

$$\Delta\Delta G = \Delta G_I - \Delta G_B \tag{11}$$

where ΔG is the free energy of solvation and the subscripts I and B represent the interfacial and bulk solution phases, respectively. It was found in our previous work (*4, 13*) that the modified Born's equation can describe the free energy of solvation satisfactorily so that

$$\Delta G_B = \frac{-E_B}{r_i + \Delta_B} \tag{12}$$

where E_B and Δ_B are constants applicable to each class of ion such as univalent alkali metal cation and univalent halide anion, and r_i is the ionic radius. Therefore, applying Eq. (12) to the free energy of solvation of ethanol, E_B and Δ_B values were generated for ethanol solvent and the results are listed in Table 4 together with data for aqueous and methanol solvent systems. Then, assuming the same expression as Eq. (12) is also applicable to the free energy of solvation in the interfacial solution phase and using Eq. (11), we obtain

$$\left(\frac{\Delta\Delta G}{\mathbf{R}T}\right)_i = \frac{1}{\mathbf{R}T}\left(-\frac{E_I}{r_i + \Delta_I}\right) - \frac{1}{\mathbf{R}T}\left(-\frac{E_B}{r_i + \Delta_B}\right) \tag{13}$$

TABLE 4
Parameters for the Modified Born Equation Applicable to Alkali Metal Cations and Halide Anions and Cellulose Acetate (CA E-398) Material in Different Solvents

Class of ions	Solvent	$E_B \times 10^{10}$ (kJ·m/mol)	$\Delta_B \times 10^{10}$ (m)	$E_I \times 10^{10}$ (kJ·m/mol)	$\Delta_I \times 10^{10}$ (m)
Alkali metal cations	Ethanol	564.4	0.661	543.5	0.652
	Methanol[a]	656.5	0.753	665.6	0.781
	Water[b]	761.5	0.890	824.7	0.976
Halide anions	Ethanol	510.0	−0.129	515.7	−0.104
	Methanol[a]	492.9	−0.179	492.7	−0.180
	Water[b]	504.2	−0.200	477.4	−0.230

[a] From Refs. *4* and *5*.
[b] From Ref. *13*.

where E_I and Δ_I are constants applicable to each class of ions and also depend on the membrane material.

For the case of uni-univalent electrolytes (M^+X^-) such as alkali halide solutes, the combination of Eqs. (10) and (13) results in

$$\ln (D_{AM}/K\delta)_{M^+X^-} = \ln C^*_{NaCl} + \frac{1}{RT}\left\{\left(\frac{E_I}{r_{M^+} + \Delta_I}\right)_{c^+} - \left(\frac{E_B}{r_{M^+} + \Delta_B}\right)_{c^+}\right\} + \frac{1}{RT}\left\{\left(\frac{E_I}{r_{X^-} + \Delta_I}\right)_{a^-} - \left(\frac{E_B}{r_{X^-} + \Delta_B}\right)_{a^-}\right\} \tag{14}$$

With respect to application of Eq. (14) to a given membrane, the quantity ln $(D_{AM}/K\delta)_{M^+X^-}$ can be obtained from experimental RO data using Eq. (8); the unknown quantities are ln C^*_{NaCl}, $(E_I)_{c^+}$, $(\Delta_I)_{c^+}$, $(E_I)_{a^-}$ and $(\Delta_I)_{a^-}$. In order to determine these five unknowns, a minimum of five values of $D_{AM}/K\delta$ for different alkali metal halide solutes are needed. In this work, the 14 different alkali halide solutes listed in Table 3 were used to determine $D_{AM}/K\delta$ values. By using these values in Eq. (14), the best fitting data for the five unknowns mentioned above were determined for each membrane sample listed in Table 1. Of these five quantities, only ln C^*_{NaCl} is a function of the porous structure of the membrane and the other four quantities depend only on the chemical nature of the membrane material and solvent. Therefore, the average values of $(E_I)_{c^+}$, $(\Delta_I)_{c^+}$, $(E_I)_{a^-}$, and $(\Delta_I)_{a^-}$ obtained from six membrane samples were calculated. The result is listed in Table 4 together with the data for other solvent systems. The values for the above four quantities were then used in Eq. (13) to determine the free energy parameters, $(-\Delta\Delta G/RT)_i$, for each of the alkali metal cations and halide anions. The data so obtained are listed in Table 5 together with data for other solvent systems. Using the $D_{AM}/K\delta$ data for LiCl given in Table 1 and the data on $(-\Delta\Delta G/RT)_i$ for Li^+ and Cl^- ions given in Table 5, the values of ln C^*_{NaCl} for all membranes listed in Table 1 were generated. Furthermore, since the solutes, which include Ca^{2+}, Sr^{2+}, NH_4^+, NO_2^-, ClO_3^-, and ClO_4^-, also include either Na^+ or Cl^- ion in the structural formula, as indicated in Table 3, and since numerical values of ln C^*_{NaCl} are also known for all six membranes involved in this work, Eq. (10) allows the calculation of $(-\Delta\Delta G/RT)_i$ for all ions mentioned above by using experimental $(D_{AM}/K\delta)$ data of salts including the above ions and the free energy parameter of either Na^+ or Cl^-. Note that six values of $(-\Delta\Delta G/RT)_i$ can be obtained for each ion. These $(-\Delta\Delta G/RT)_i$ data were further averaged

TABLE 5
Free Energy Parameters of Ions Applicable to Ethanol, Methanol, and Water Solvents and Cellulose Acetate (CA E-398) Material at 25°C

		$-\Delta\Delta G/\mathbf{R}T$		
		Solvent		
Ion	Ionic radius[a]	Ethanol	Methanol[c]	Water
Li^+	0.60	−5.40	−1.36	5.77[d]
Na^+	0.95	−4.45	−0.43	5.79
K^+	1.33	−3.72	0.03	5.91
Rb^+	1.43	−3.49	0.14	5.86
Cs^+	1.69	−3.22	0.24	5.72
NH_4^+	—	−5.28	−0.19	5.97[e]
Mg^{2+}	0.65	—	−2.92	8.72[e]
Ca^{2+}	0.99	−6.06	−2.30	8.88[e]
Sr^{2+}	1.13	−6.07	−2.59	8.76[e]
Ba^{2+}	1.35	—	−2.60	8.50[e]
F^-	1.36	−1.72	−2.34	−4.91[d]
Cl^-	1.81	−0.61	−1.71	−4.42[d]
Br^-	1.95	−0.43	−1.58	−4.25[d]
I^-	2.16	−0.25	−1.41	−3.98[d]
NO_2^-	2.60[b]	−0.01	−2.04	−3.85[d]
NO_3^-	2.66[b]	—	−1.54	−3.66[d]
ClO_3^-	2.75[b]	0.58	−1.20	−4.10[d]
ClO_4^-	2.90[b]	0.70	−1.69	−3.60[d]
BrO_3^-	3.14[b]	—	−1.38	−4.89[d]

[a] From Ref. *16*.
[b] From Ref. *17*.
[c] From Refs. *4–6*.
[d] From Ref. *13*.
[e] From Ref. *14*.

out. The results are shown in Table 5 together with the values for other solvent systems.

Using the data of $\ln C^*_{\mathrm{NaCl}}$ listed in Table 1 in Eq. (10) and the data on $(-\Delta\Delta G/\mathbf{R}T)_i$ for different ions given in Table 5, the values of $D_{AM}/K\delta$ for all the solutes involved in this study can be calculated for each membrane. Using these values of $D_{AM}/K\delta$ in Eq. (8), the values of f (solute separation) for different solutes were calculated and compared with the actual experimental data for each film. The excellent agreement between the calculated and experimental data on solute separation shown in Table 6 confirms the practical validity of the free energy parameter given in Table 5 for ethyl alcohol solvent systems.

Equation (10) assumes the total dissociation of the inorganic salts in the solvent. In the absence of reliable data on dissociation constants of inorganic salts in ethanol, this assumption was necessary for the calculation of the free energy parameter.

Comparison of Free Energy Parameters Obtained for Water, Methanol, and Ethanol Solvents

As explained, $\Delta\Delta G$ data reflect the interaction force working in the membrane material–solute–solvent system and a systematic change in such interaction forces is expected with the change in the dielectric constant of the solvent. Therefore, it may be interesting to compare the free energy parameters which have been generated for water, methanol, and ethanol solvants. Such a comparison is presented in the form of $\Delta(-\Delta\Delta G/\mathbf{R}T)_i$ versus ionic radius in Figs. 1 and 2 for different univalent cations and univalent anions, respectively. The quantity $\Delta(-\Delta\Delta G/\mathbf{R}T)_i$ is defined as

$$\Delta(-\Delta\Delta G/\mathbf{R}T)_i = (-\Delta\Delta G/\mathbf{R}T)_i - (-\Delta\Delta G/\mathbf{R}T)_{\mathrm{Na^+\ or\ Cl^-}} \tag{15}$$

where the subscripts Na^+ and Cl^- are applicable to univalent cations and univalent anions, respectively. The reason for considering the $(-\Delta\Delta G/\mathbf{R}T)_i$ values relative to reference sodium or chloride ion rather than absolute $(-\Delta\Delta G/\mathbf{R}T)_i$ values is because experimentally obtained $(-\Delta\Delta G/\mathbf{R}T)_i$ values are more reliable as relative quantities. Figure 1 clearly indicates that the difference in the value of $(-\Delta\Delta G/\mathbf{R}T)_i$ among cations under study is widened considerably as the dielectric constant of solvent decreases from water to ethanol. The same tendency is observed for anions, as indicated in Fig. 2.

The reason for the enhanced difference in the value of relative free energy parameters exhibited among ions when the solvent dielectric constant is low is at present not clear. The generality of the principle has to be further confirmed by studying the separation of inorganic solutes from some other solvents of even lower dielectric constant. It should be pointed out, however, that the above tendency in the relative free energy parameter is faithfully

TABLE 6
Comparison of Experimental and Calculated Reverse Osmosis Separations[a]

	Membranes											
	1		2		3		4		5		6	
	Solute separation (%)											
Solute	Exptl	Calc	Exptl	Calc	Exptl	Calc	Exptl	Calc	Exptl	Calc	Exptl	Calc
LiCl	96.1	94.6	97.3	94.1	96.5	93.7	90.2	91.9	94.2	92.6	91.5	90.6
LiBr	94.3	93.6	96.8	93.0	93.9	92.6	—	90.6	90.1	91.4	89.1	89.0
NaCl	87.3	87.4	87.3	86.4	85.3	85.7	82.7	82.2	81.4	83.6	79.1	79.7
NaBr	82.6	85.5	85.2	84.4	—	83.7	—	79.7	83.5	81.3	78.2	77.1
NaI	83.1	83.1	83.1	82.0	82.6	81.1	79.5	76.7	—	78.5	76.9	73.9
KF	89.5	91.1	92.5	90.4	88.3	89.9	88.4	87.2	87.8	88.3	87.2	85.7
KCl	81.5	77.6	79.4	76.1	77.1	75.2	74.1	69.8	76.5	72.0	—	66.6

KBr	77.9	74.4	—	72.9	72.1	71.9	71.1	66.0	73.2	68.4	—	62.8
KI	74.1	71.1	70.9	69.5	70.1	68.5	67.7	62.3	66.9	64.8	—	59.0
RbBr	70.2	70.2	68.6	68.6	65.3	67.5	63.6	61.2	63.6	63.8	58.7	57.9
RbI	66.1	66.4	62.5	64.7	60.7	63.6	60.7	57.0	57.1	59.8	55.4	53.8
CsCl	61.2	68.1	60.3	66.4	64.7	65.4	59.4	58.9	61.2	61.6	51.7	55.6
CsBr	68.8	64.3	62.3	62.5	64.8	61.4	59.8	54.7	62.3	57.5	—	51.4
CsI	54.5	60.4	—	58.6	52.1	57.5	51.2	50.6	51.2	53.5	48.8	47.4
NH_4Cl	96.7	94.2	94.5	93.7	92.8	93.3	91.2	91.5	90.1	92.2	86.2	90.2
$CaCl_2$	97.2	97.1	98.7	96.8	98.5	96.5	92.2	95.6	96.7	95.9	91.3	94.7
$SrCl_2$	97.5	97.1	97.9	96.8	97.4	96.6	93.9	95.6	96.2	96.0	92.8	94.8
$NaNO_2$	78.1	79.3	74.0	77.9	74.0	76.9	73.6	71.8	70.8	73.8	67.3	68.6
$NaClO_3$	67.5	68.5	70.6	66.7	64.8	65.5	—	59.2	53.4	61.7	52.6	55.6
$NaClO_4$	68.2	66.2	58.2	64.4	65.8	63.3	—	56.7	53.7	59.4	—	53.2

[a] Solute concentration in feed, ~0.001 molal. Operating pressure, 1724 kPag (=250 psig).

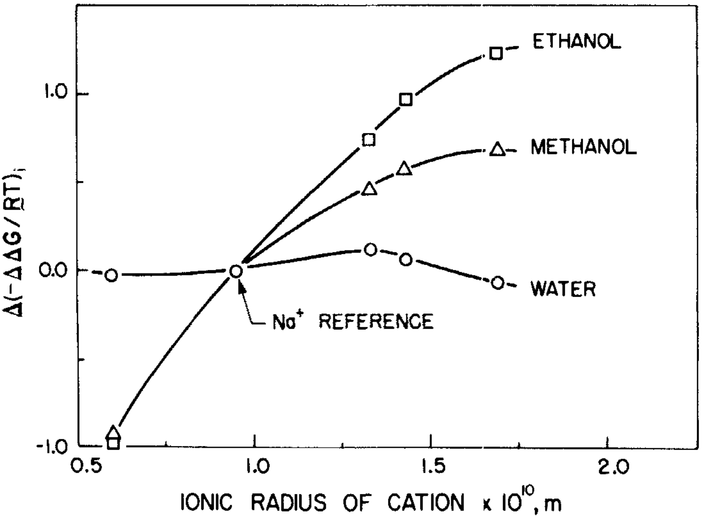

Fig. 1. $\Delta(-\Delta\Delta G/\mathbf{R}T)$ vs r_i correlation with respect to univalent cations in different solvents.

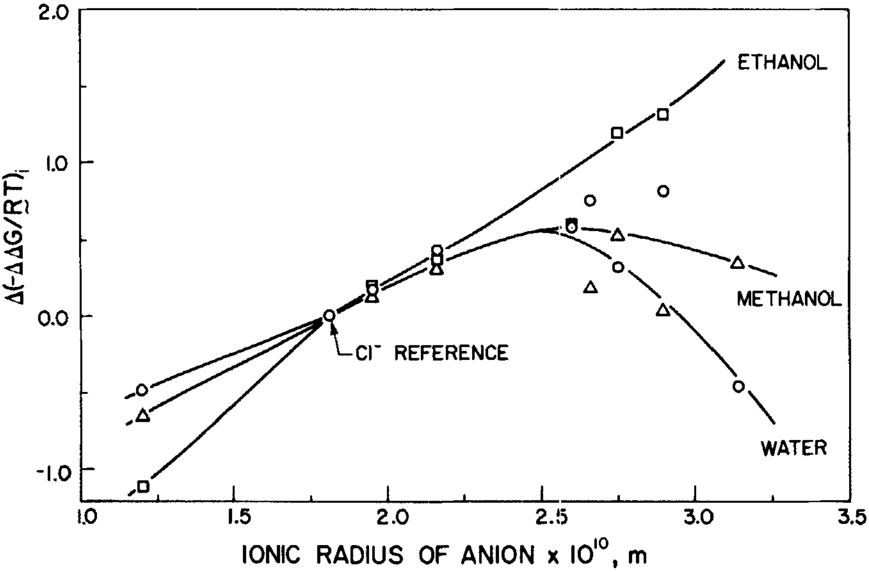

Fig. 2. $\Delta(-\Delta\Delta G/\mathbf{R}T)$ vs r_i correlation with respect to univalent anions in different solvents.

reflected in the reverse osmosis separation data. For example, Table 7 shows the separation of various inorganic solutes from water, methanol, and ethanol solutions. In order to make the comparison of different solvents easier, a membrane which gives approximately equal sodium chloride separation (~80%) was chosen for each solvent, and the data obtained for other solutes using the particular membranes chosen are listed in the table. Table 7 clearly indicates that the difference in solute separation data among inorganic solutes widens considerably as the solvent is changed progressively from a high dielectric constant (water) to a low dielectric constant (ethanol). This implies that the fractionation of different inorganic solutes is accomplished most easily in the last solvent. This information has practical significance when the membrane process is applied for the fractionation of various inorganic solutes.

TABLE 7

Comparison of Inorganic Solute Separation by Cellulose Acetate Membranes of Similar NaCl Separations in Water, Methanol, and Ethanol Solvent[a]

	Solvent		
	Water	Methanol	Ethanol
Solute	Solute separation (%)		
LiCl	82.2	87.6	91.1
LiBr	77.4	88.8	90.7
NaCl	83.2	80.3	81.4
NaBr	81.6	70.4	83.5
NaI	76.3	75.9	70.3
KF	89.5	77.4	66.2
KCl	82.9	67.8	76.5
KBr	81.0	64.2	73.2
KI	—	62.3	66.9
RbCl	86.3	73.2	—
RbBr	83.2	—	63.6
RbI	—	—	57.1
CsCl	87.5	67.0	61.2
CsBr	84.2	62.3	62.3
CsI	—	—	51.2

[a] Solute concentration in feed ~0.001 molal. Operating pressure, 1724 kPag (= 250 psig).

CONCLUSION

The following conclusions can be obtained from the experimental results in this work and the analysis thereof.

1) Inorganic solutes can be separated efficiently from ethanol solutions by applying porous cellulose acetate reverse osmosis membranes.

2) General transport equations based on Kimura-Sourirajan analysis and the free energy parameter approach to the ionic contribution to the solute transport parameter are both valid in the case of ethanol solvent. Thus, the physicochemical principles involved in the separation of inorganic solutes from ethanol solution are the same as those governing in the aqueous solutions.

3) The difference in free energy parameters among univalent cations and univalent anions is even more enhanced in ethanol solvent than in methanol solvent. This may be due to the even lower dielectric constant of ethanol solvent.

SYMBOLS

A	pure solvent permeability constant (kg·mol ethanol/m^2·s·kPa)
$\ln C^*_{NaCl}$	parameter representing the porosity on membrane surface
c	molar density of solution (mol/m^3)
D_{AB}	diffusivity of solute in ethanol (m^2/s)
$D_{AM}/K\delta$	solute transport parameter (treated as a single quantity), (m/s)
E_B, E_I	quantities involved in the modified Born equation of solvation free energy (kJ·m/mol)
f	fraction solute separation
ΔG_B	free energy of solvation of solute in the bulk solution phase (kJ/mol)
ΔG_I	free energy of solvation of solute in the interfacial solution phase (kJ/mol)
$-\Delta\Delta G/\mathbf{R}T$	free energy parameter for the ion at 25°C
k	mass transfer coefficient for the solute on the high pressure side of the membrane (m/s)
M_B	molecular weight of solvent ethanol
N_B	flux of solvent ethanol through membrane (mol/m^2·s)
n_a, n_c	number of moles of anions and cations respectively arising from ionization of 1 mol of solute

P	operating pressure (kPa)
(PR)	product rate through given area of membrane surface (kg/h)
(PSP)	pure solvent permeation rate through given area of membrane surface (kg/h)
$\mathbf{R}$	gas constant
r_i	ionic radius (m)
S	effective membrane area (m^2)
T	absolute temperature (°K)
X_A	mole fraction of solute

Greek Letters

Δ_B, Δ_I	quantities involved in the modified Born equation of solvation free energy (m)
ρ	solution density (kg/m^3)
π	osmotic pressure (kPa)

Subscripts

1	bulk solution phase
2	concentrated boundary solution on the high pressure side of the membrane
3	membrane permeated product solution on the low pressure side of the membrane

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